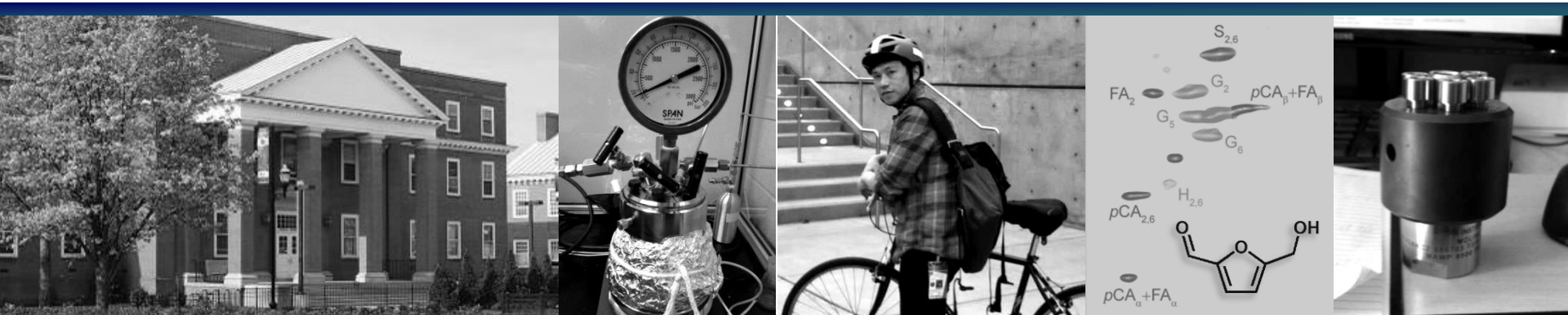


# Renewable fuels and chemicals from municipal solid waste

**Noppadon Sathitsuksanoh (Tik)**

*Chemical Engineering  
University of Louisville  
August 2<sup>nd</sup>, 2016*

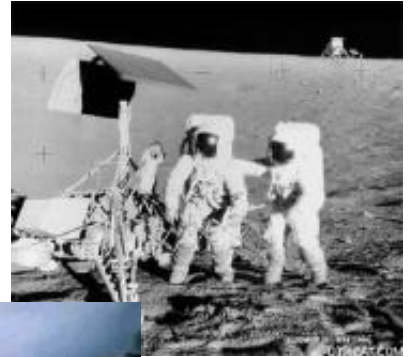


# Reliance of imported energy represents a significant cost and energy supply risk

*Cost of Oil imports (2010) is equivalent to*



\$300 B  $\approx$  2 x Apollo Space Program



\$135 B  $\approx$  Three  
5 x Gorges  
Dam



\$300 B  $\approx$  20 x Channel Tunnel

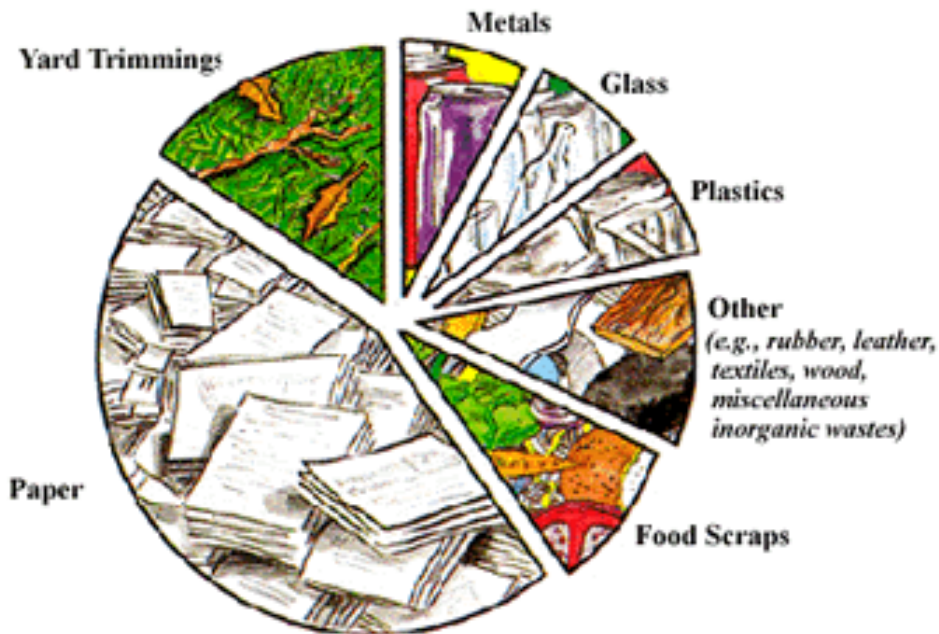


All costs in US\$<sub>2011</sub>

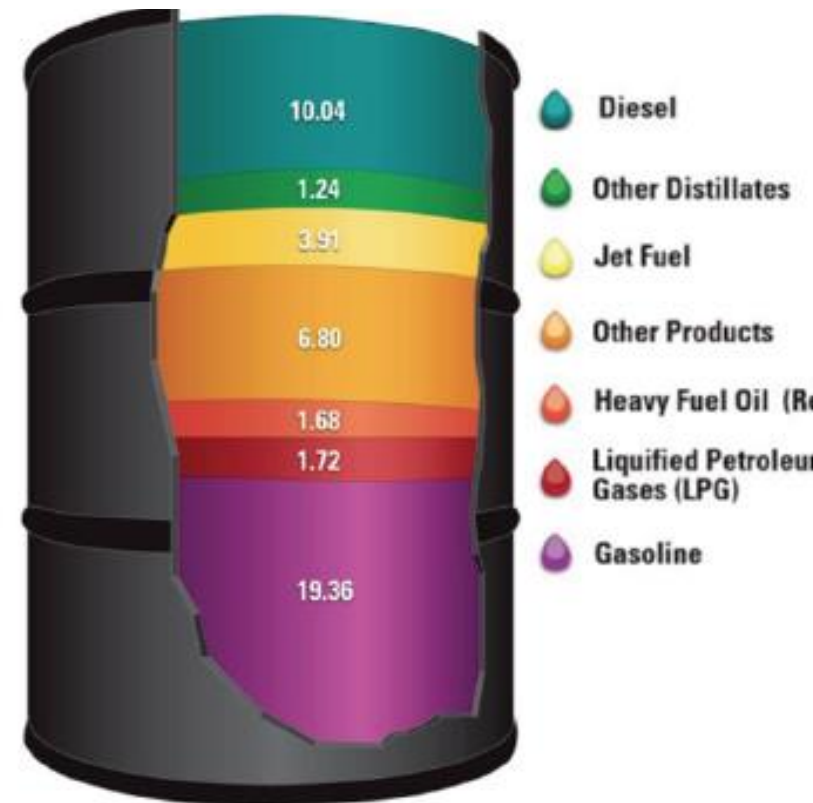
Sources: IEA, WhatItCosts.com, Wikipedia, CFO.com Magazine, USInflationCalculator.com

# MSW can be used to supplement products from crude oil

Municipal solid waste



Crude oil



# Background & Experiences

SIU Southern Illinois University  
CARBONDALE



2007

2008

2009

2010

2011

2012

2013

2014

2015

## Electrocatalysis

- Ni alloys
- Electrodeposition

## Fuels reforming

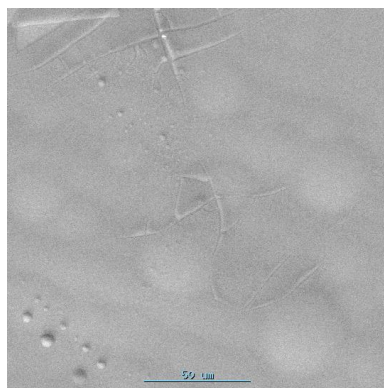
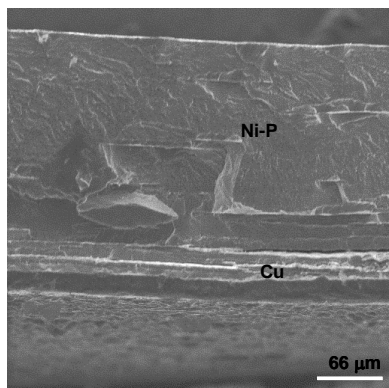
- JP5/JP8 to  $H_2$
- $H_2$  for PEMFCs to power radar

## Lignocellulose processing

- Enzymatic bio-fuel cells
- NMR

## Catalytic upgrading of transgenic plants

## Advanced Renewable Materials (ARM) Lab



(*J. Mater. Sci. Lett.* (2003) **20**: 1092)

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(*J. Power Sources* (2007) **173**: 478)

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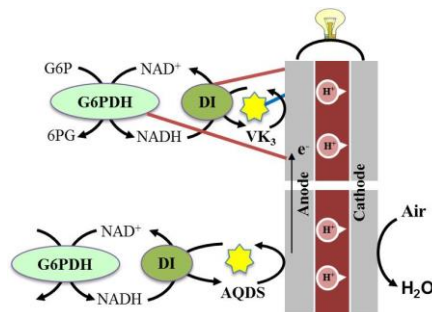
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(PNAS (2013) 10: 7182)

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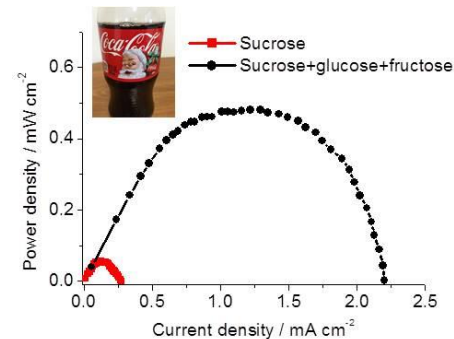
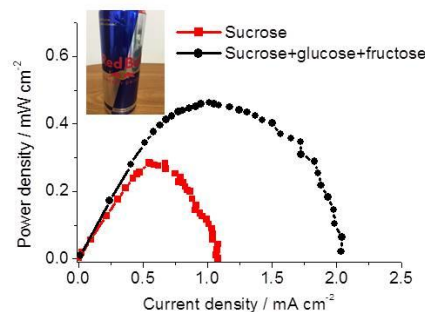
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(PNAS (2013) 10: 7182)

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jbei  
Joint BioEnergy Institute



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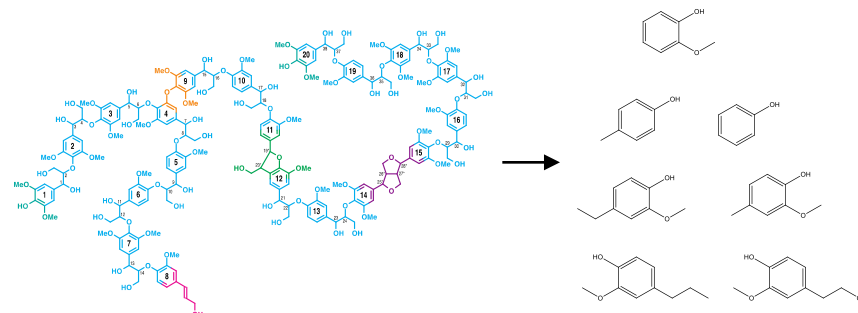
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- NMR

## Catalytic upgrading of lignocellulose

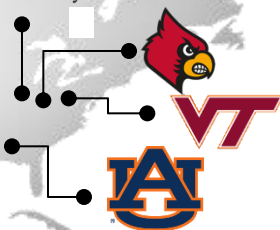
## Advanced Renewable Materials (ARM) Lab



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jbei  
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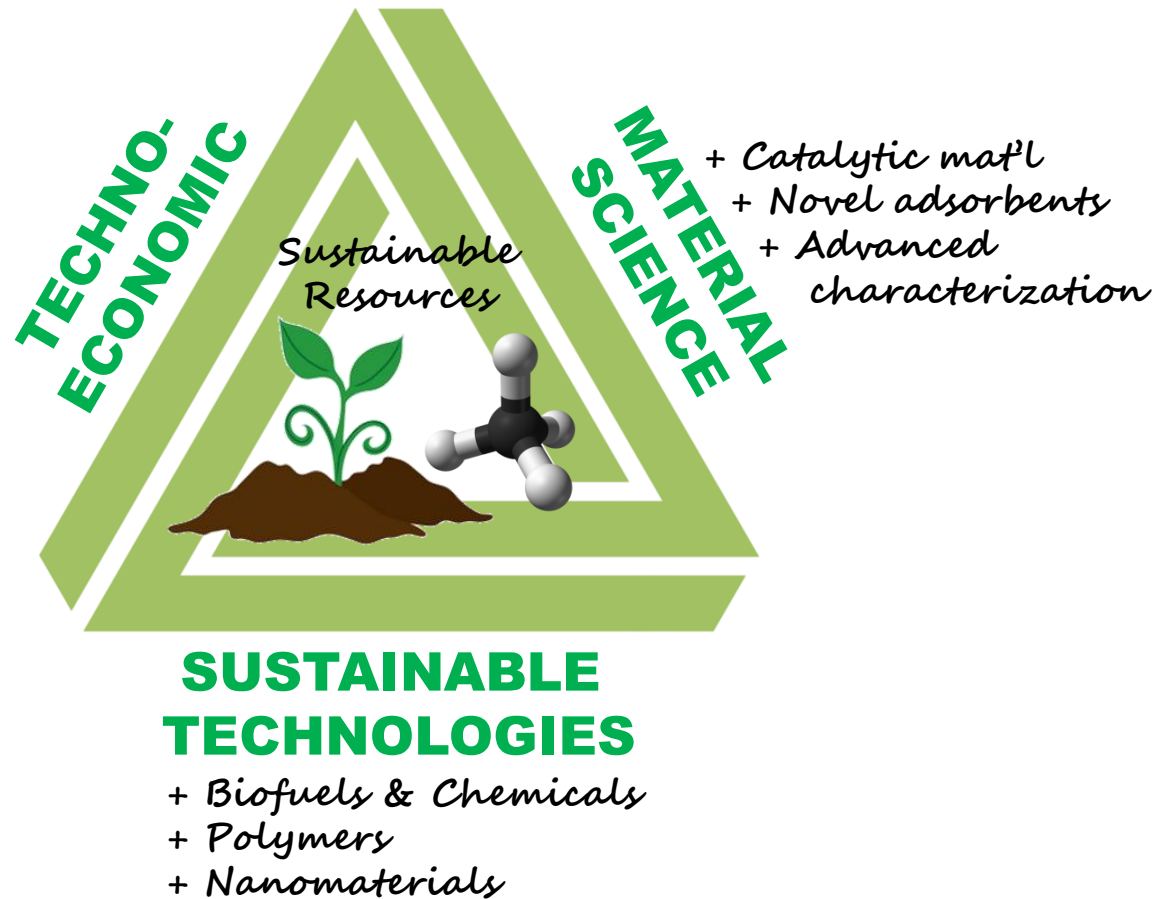
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## Catalytic upgrading of lignocellulose

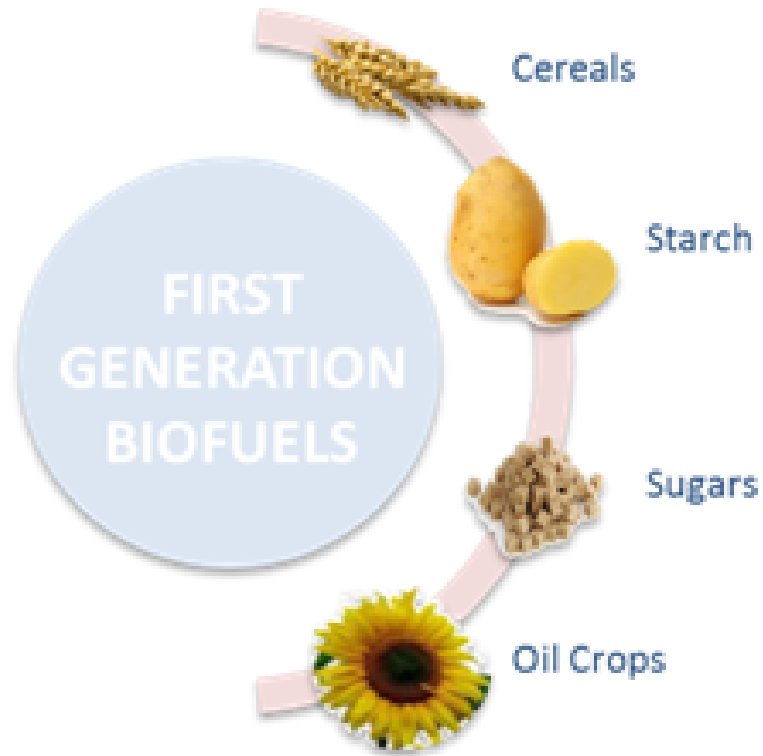
## Advanced Renewable Materials (ARM) Lab



# We look at resources, processes, and economics to find solutions



# 1<sup>st</sup> generation biofuels are derived from food crops



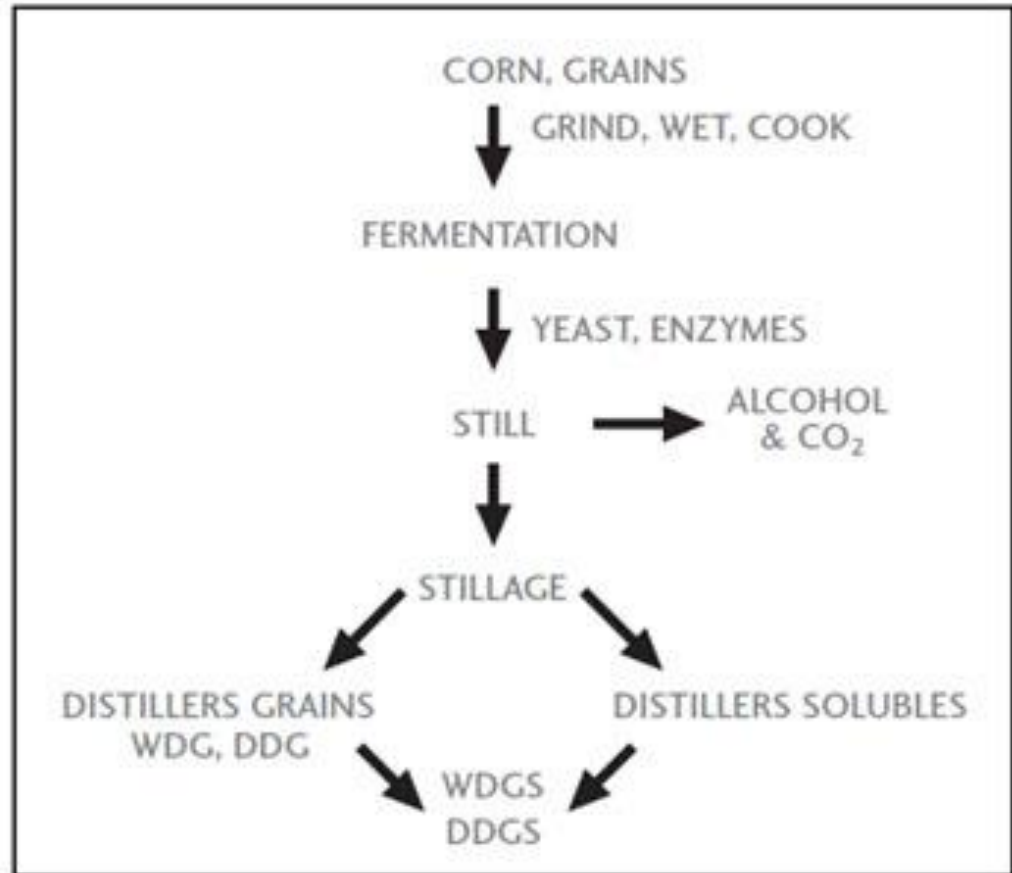
# 1<sup>st</sup> generation biofuels from food crops drive up the food price

**PRO**

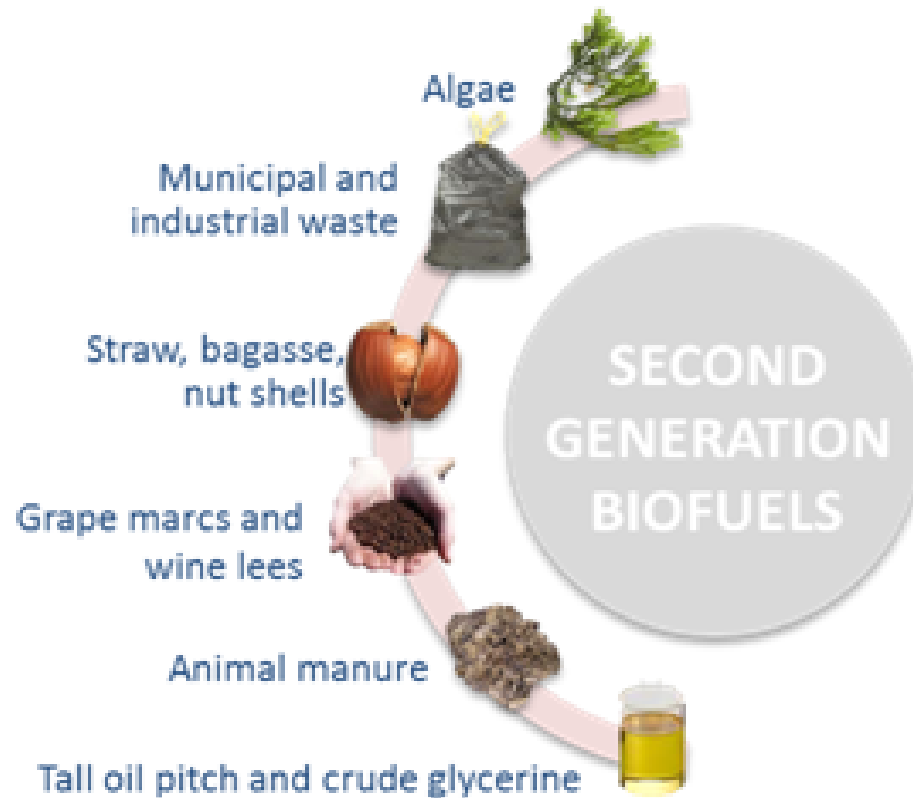
*Easy to be converted*

**CON**

*Competitive to food price*



# 2<sup>nd</sup> generation biofuels from non-food crops are more sustainable and scalable



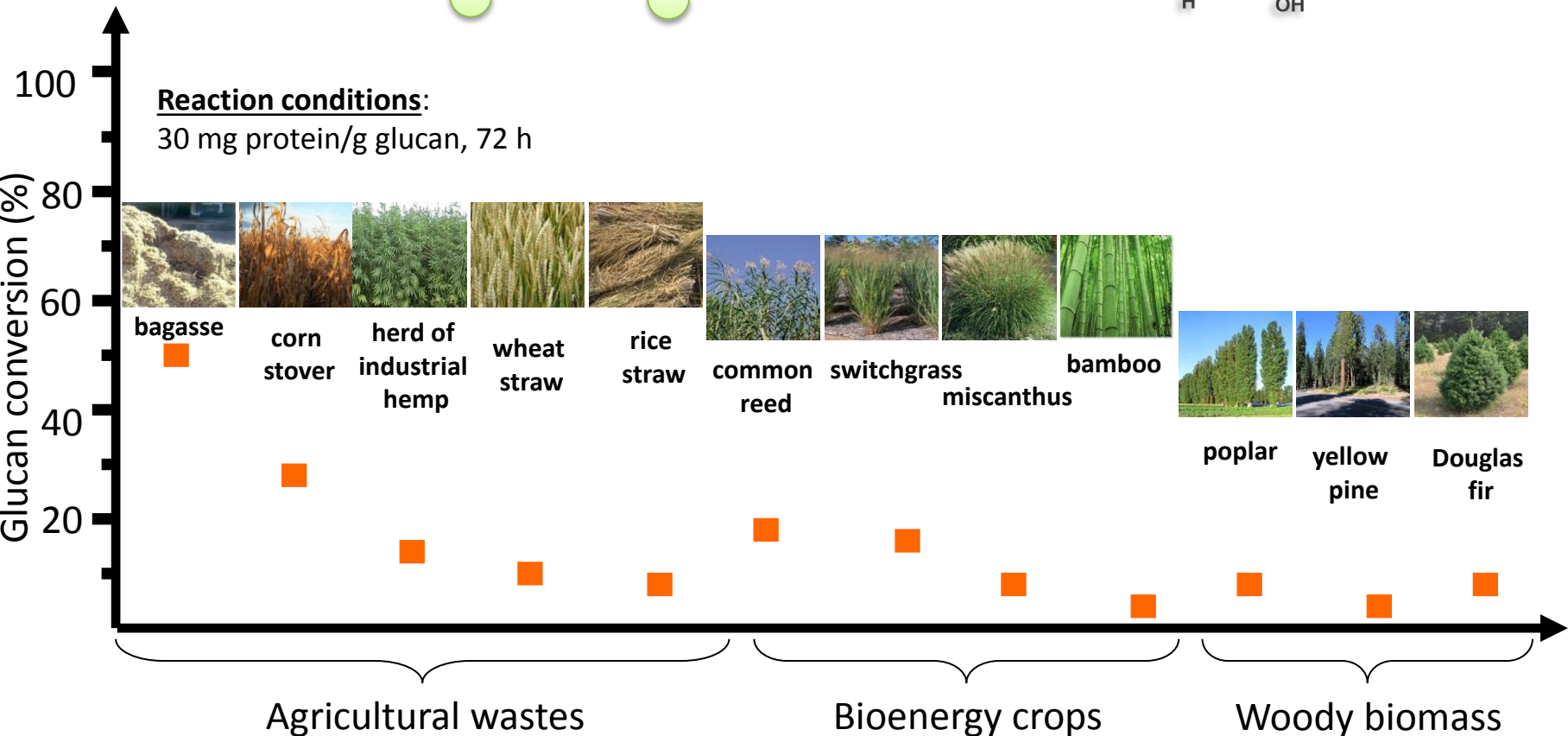
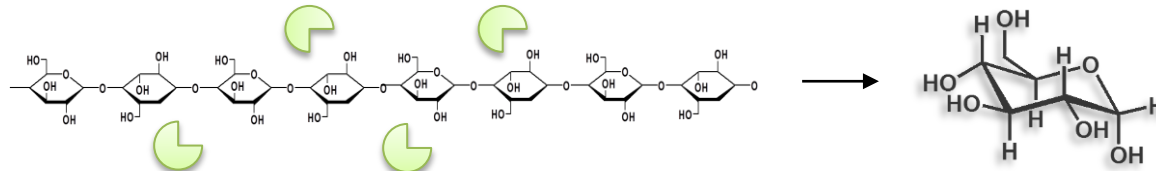
## **PRO**

*Low cost  
Low carbon  
Scalable  
Sustainable*

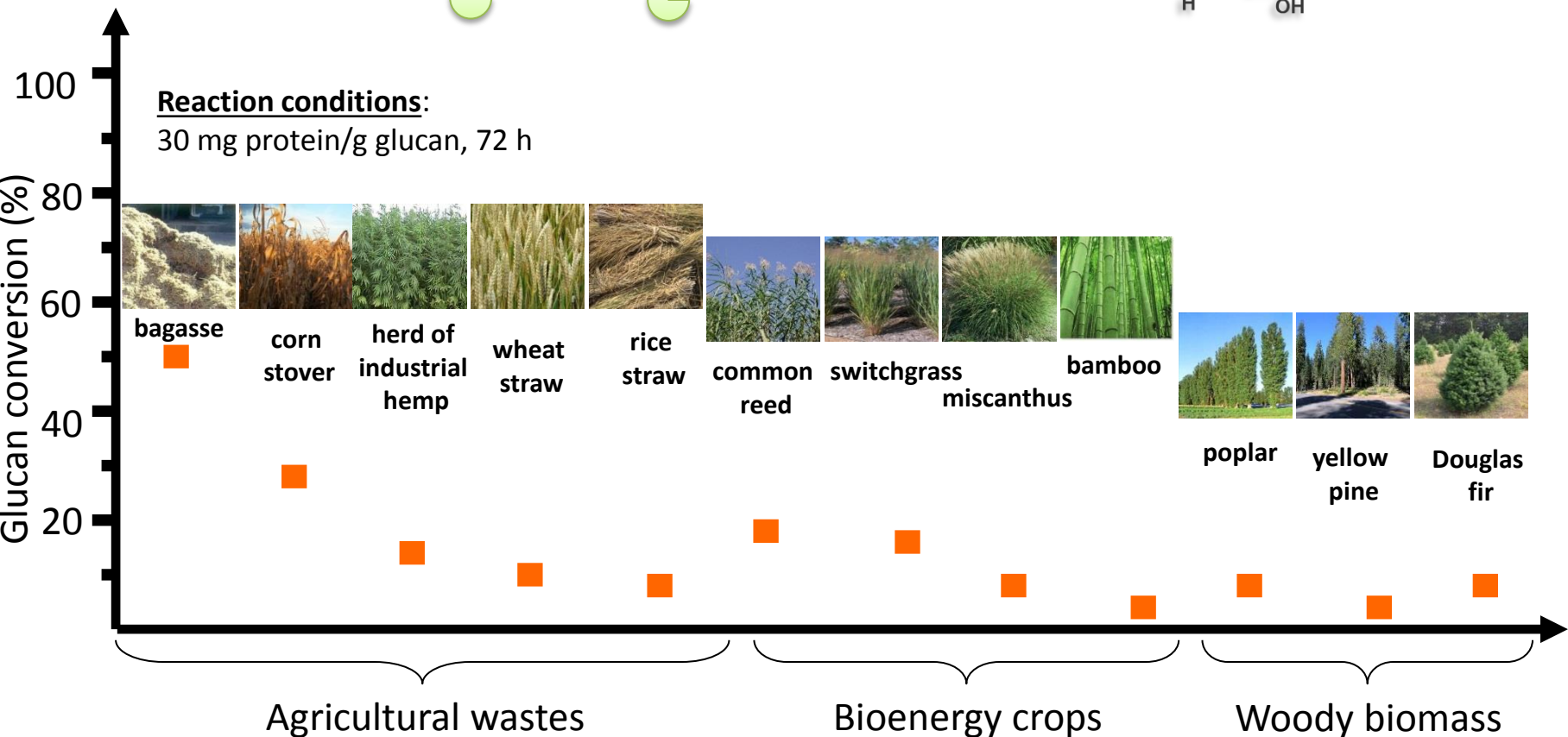
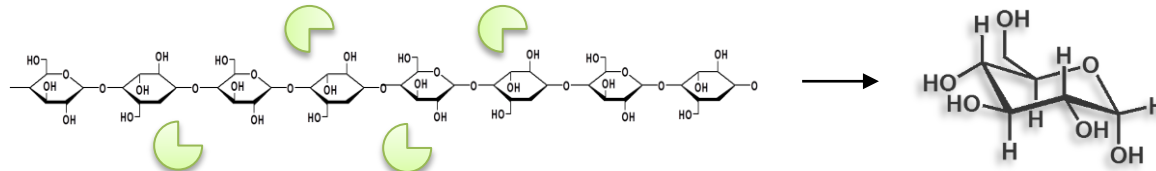
## **CON**

*Complex structure  
Hard to digest by  
enzymes\microbes*

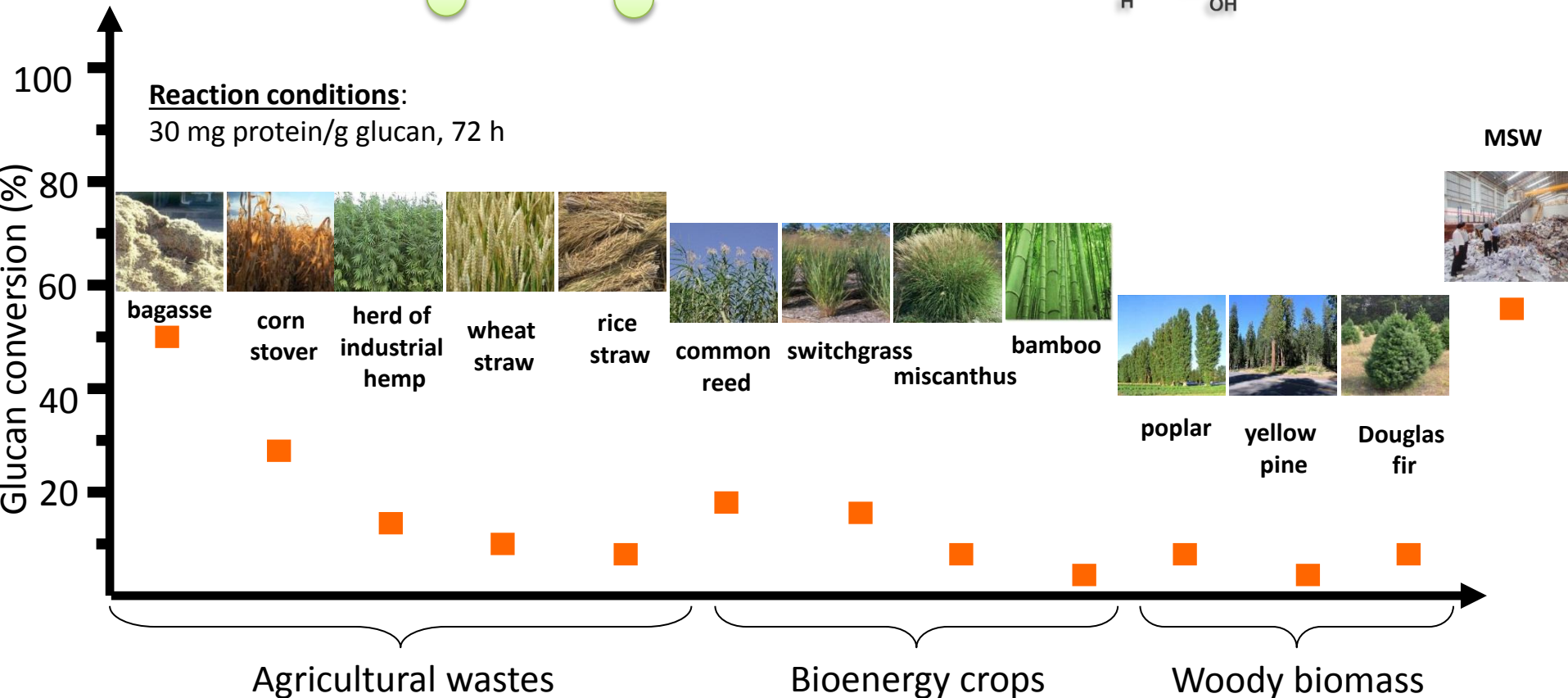
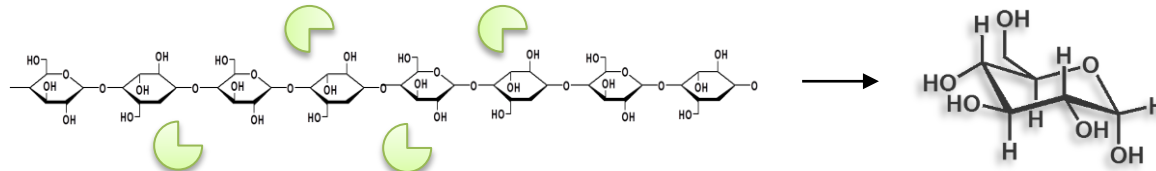
# Corn stock, husk, and leaves are hard for enzymes to digest and normally left unused



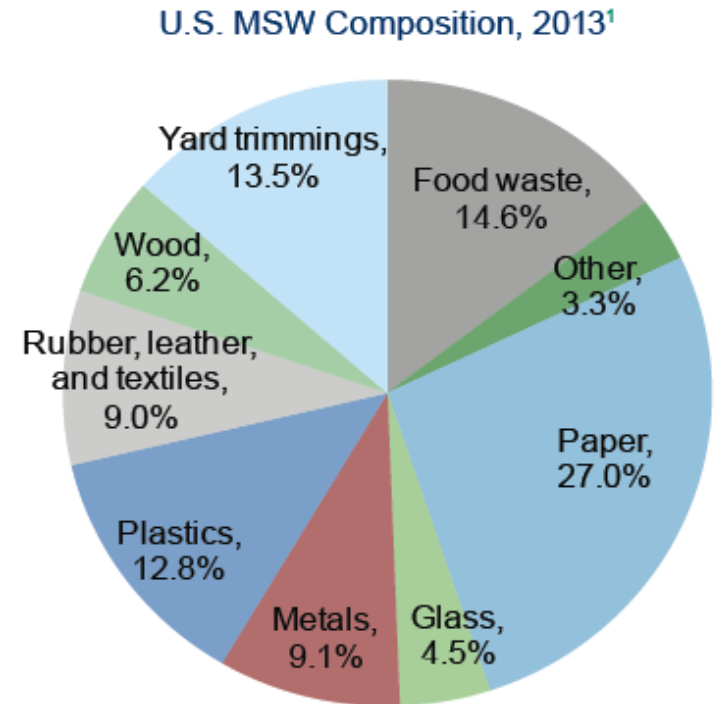
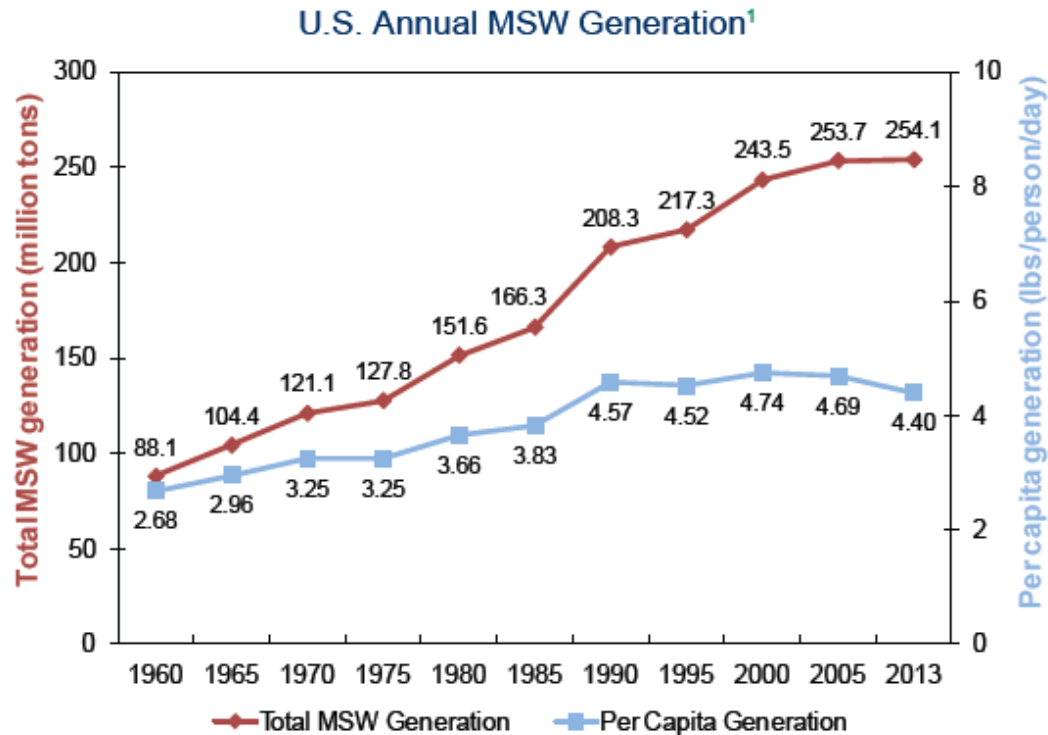
# DOE 2016 billion ton study shows that agricultural waste alone cannot meet the fuel demand



# DOE 2016 billion ton study shows that agricultural waste alone cannot meet the fuel demand



# In 2013, ~70 million tons of paper wastes were generated. They derived from plants



# The blend of agricultural waste and paper waste have a great potential to fuel the U.S.



**Agricultural waste**



**Paper waste**

**UPGRADING**

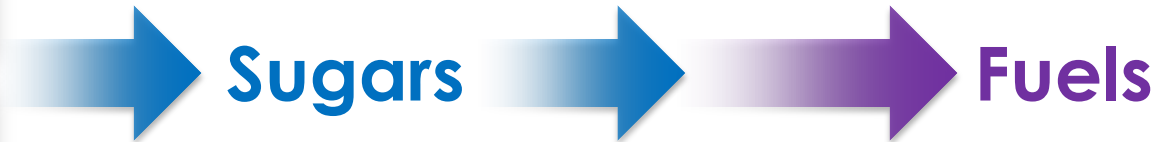


**Transportation fuels**

# Outline



**Plant-based  
waste**



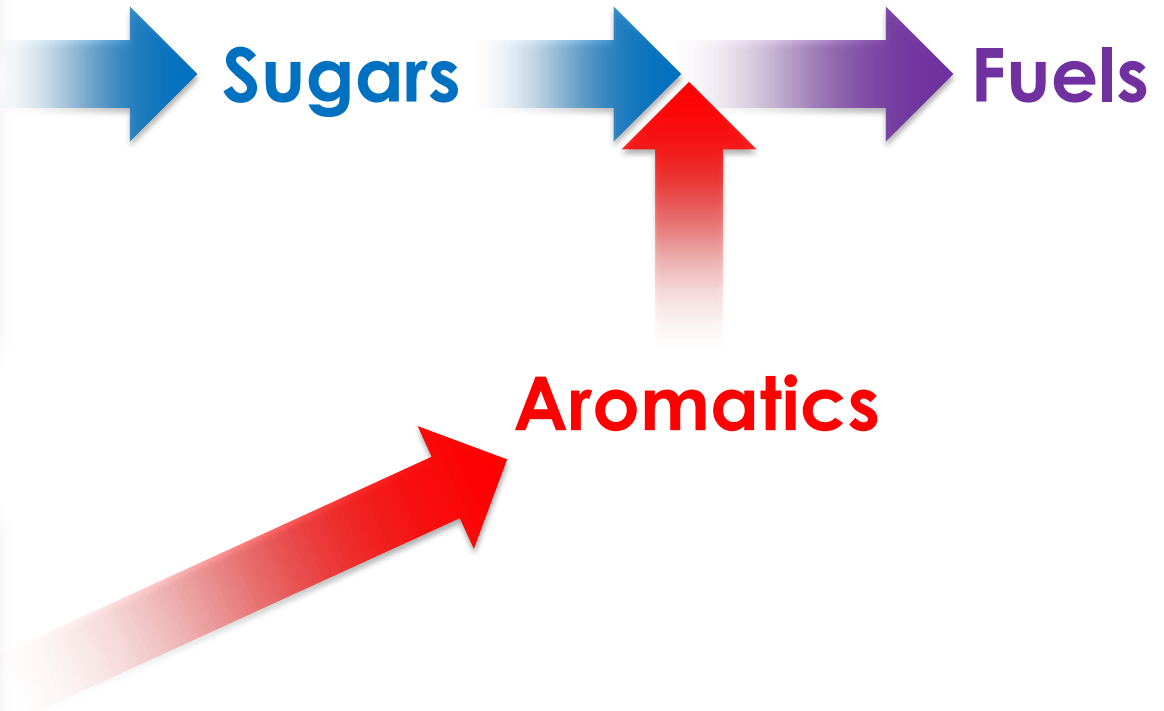
# Outline



**Plant-based  
waste**

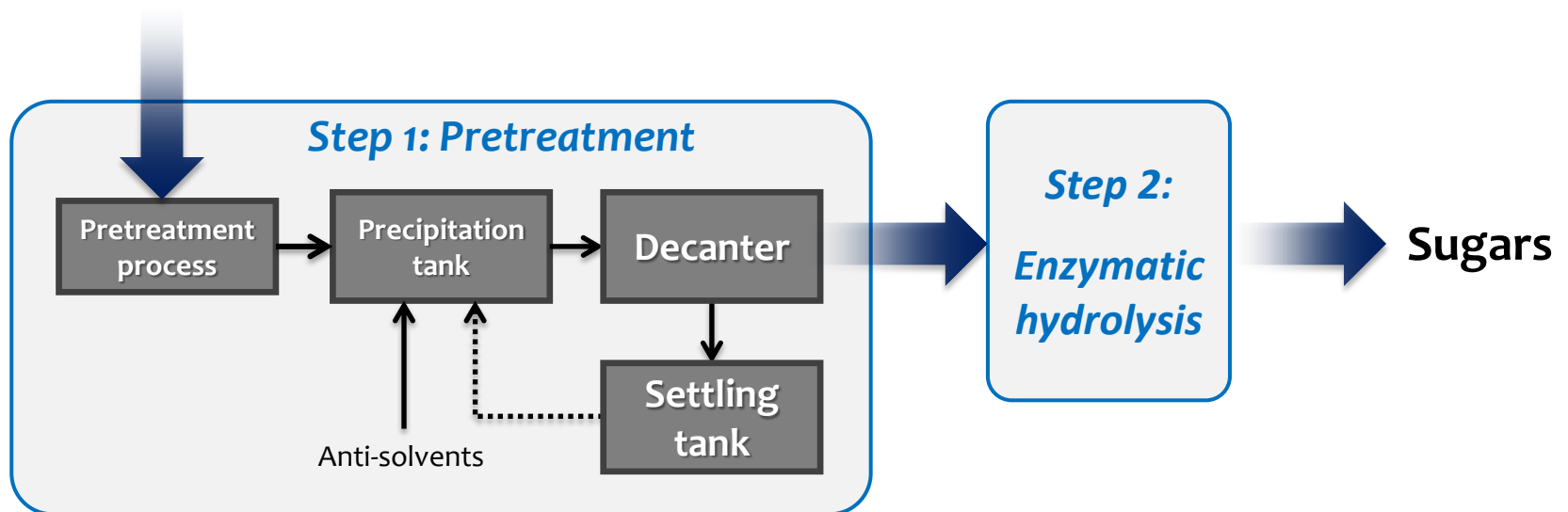


**Tire waste**

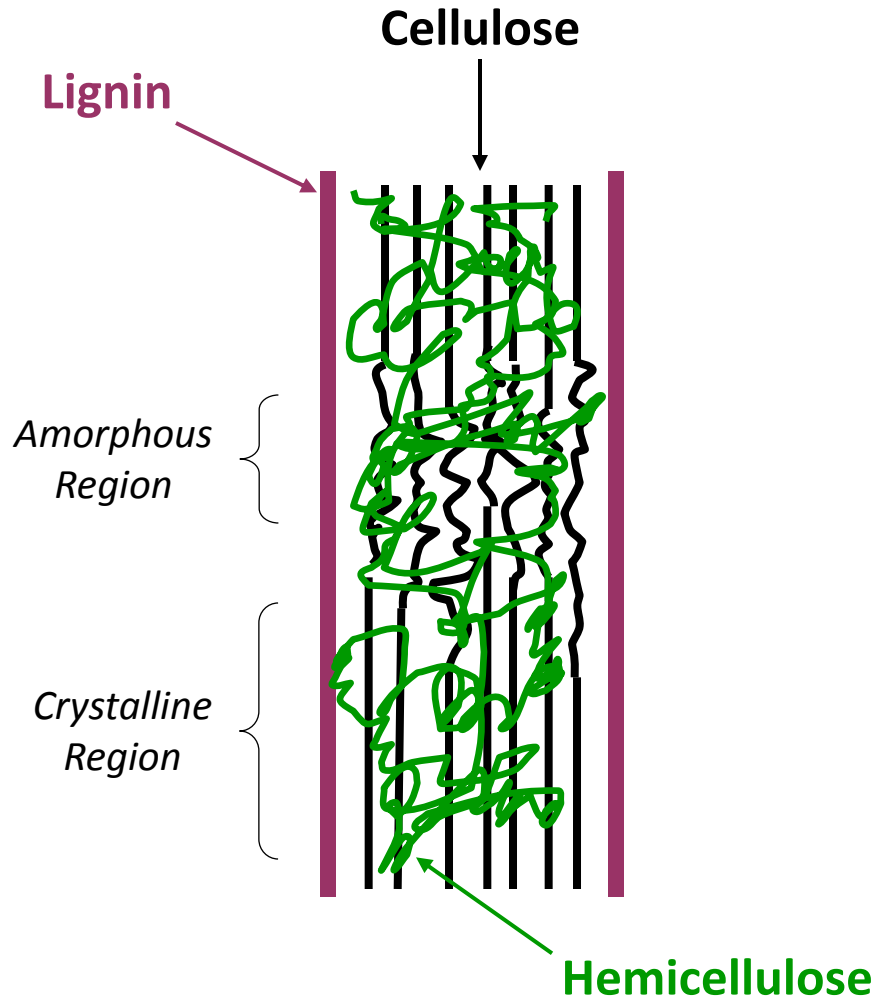


# Unlocking sugars from biomass involves 2 steps: pretreatment and enzymatic hydrolysis

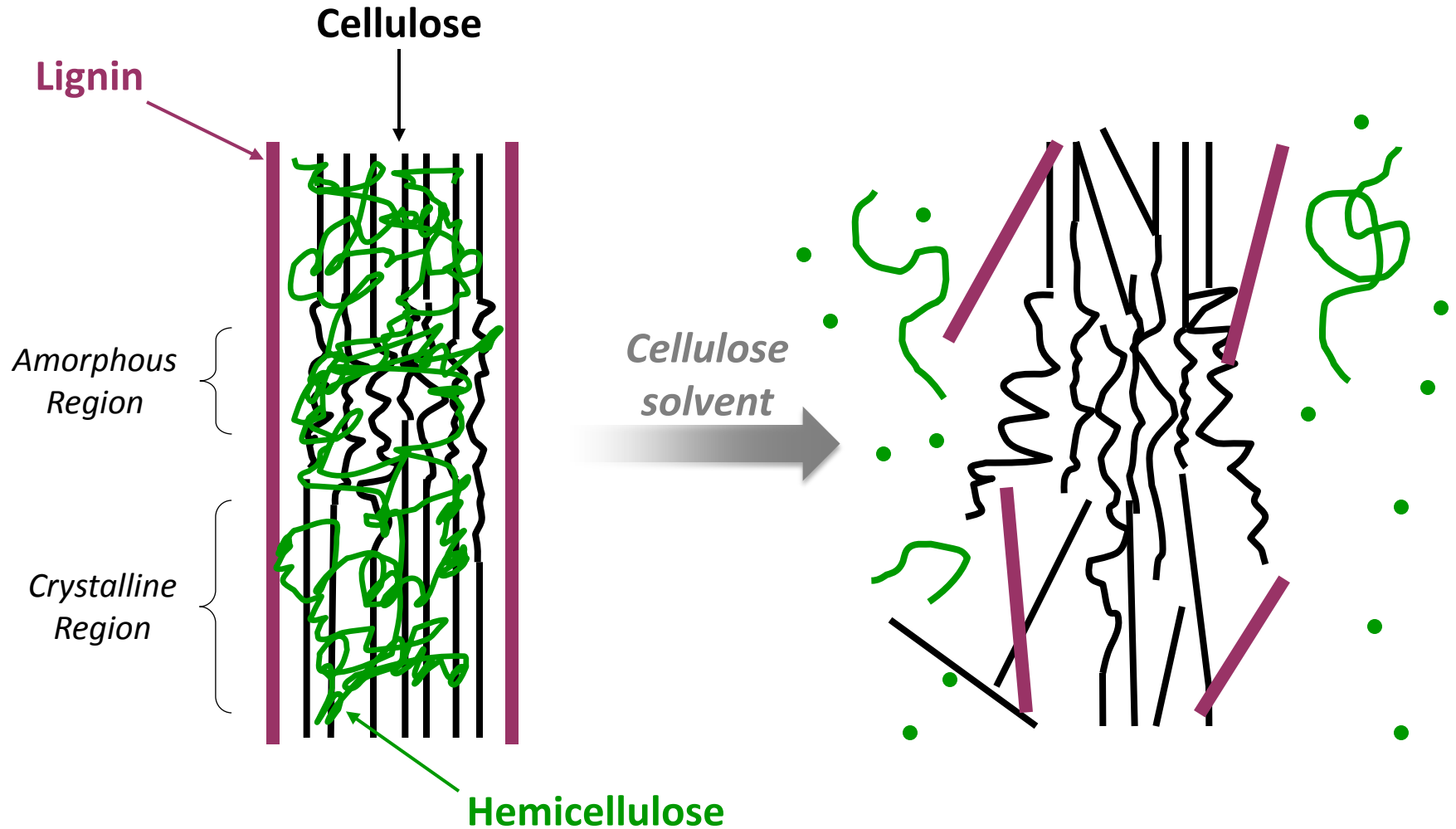
MSW + Corn stover (1:1)



# Paper waste is derived from plant. Complex structure makes it difficult to release sugars



# Cellulose solvent process breaks tough barrier and unlock sugars



# Effect of pretreatments on MSW structures



MSW + CS

DA



0.5 %  $\text{H}_2\text{SO}_4$ , 20 min, 160 °C

SAA



15%  $\text{NH}_3$ , 24 h, 60 °C

COSLIF



85%  $\text{H}_3\text{PO}_4$ , 30 min, 50 °C

IL



100% BMIM[Cl],  
30 min, 105 °C

ABENGOA BIOENERGY

POET™  
Energy inspired.™

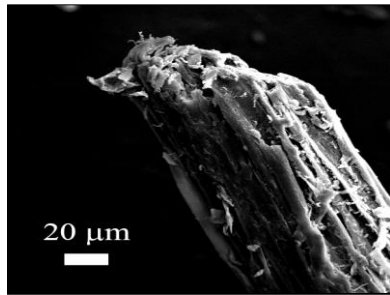


DANISCO.

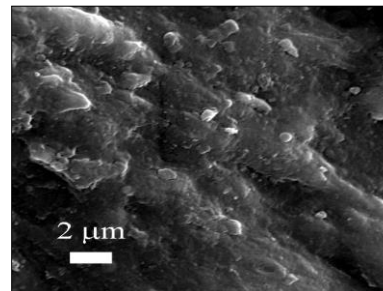
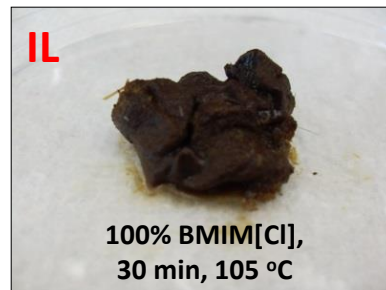
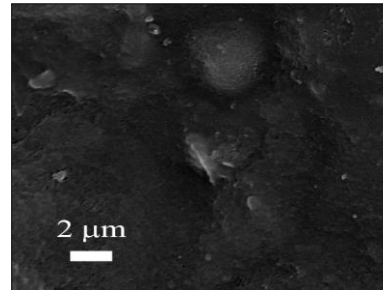
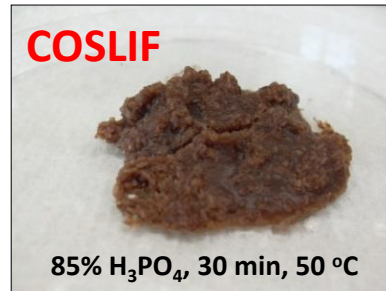
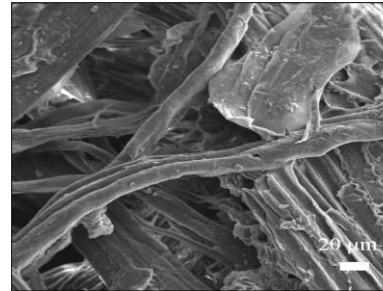
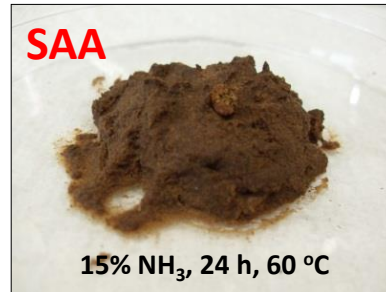
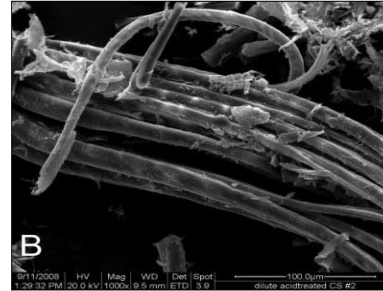


OPTAFUEL

# Effect of pretreatments on lignocellulose structures



MSW + CS



ABENGOA BIOENERGY

POET™  
Energy inspired.™

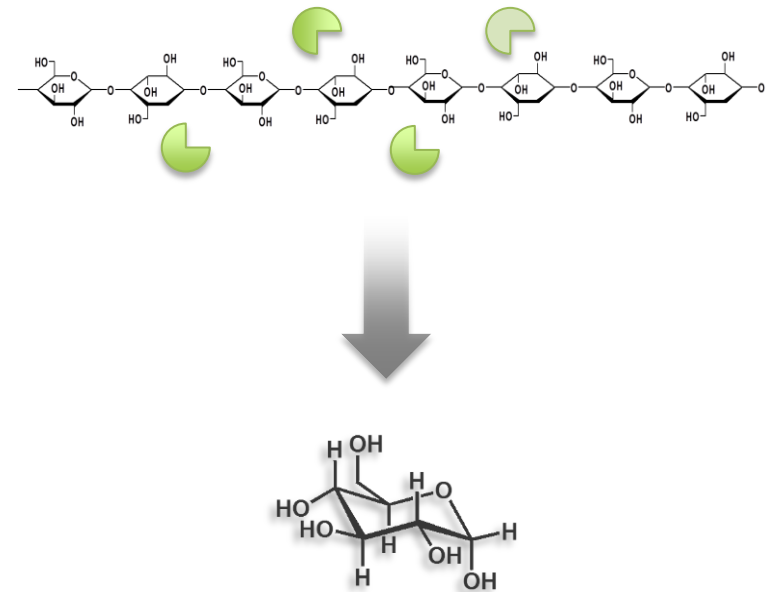
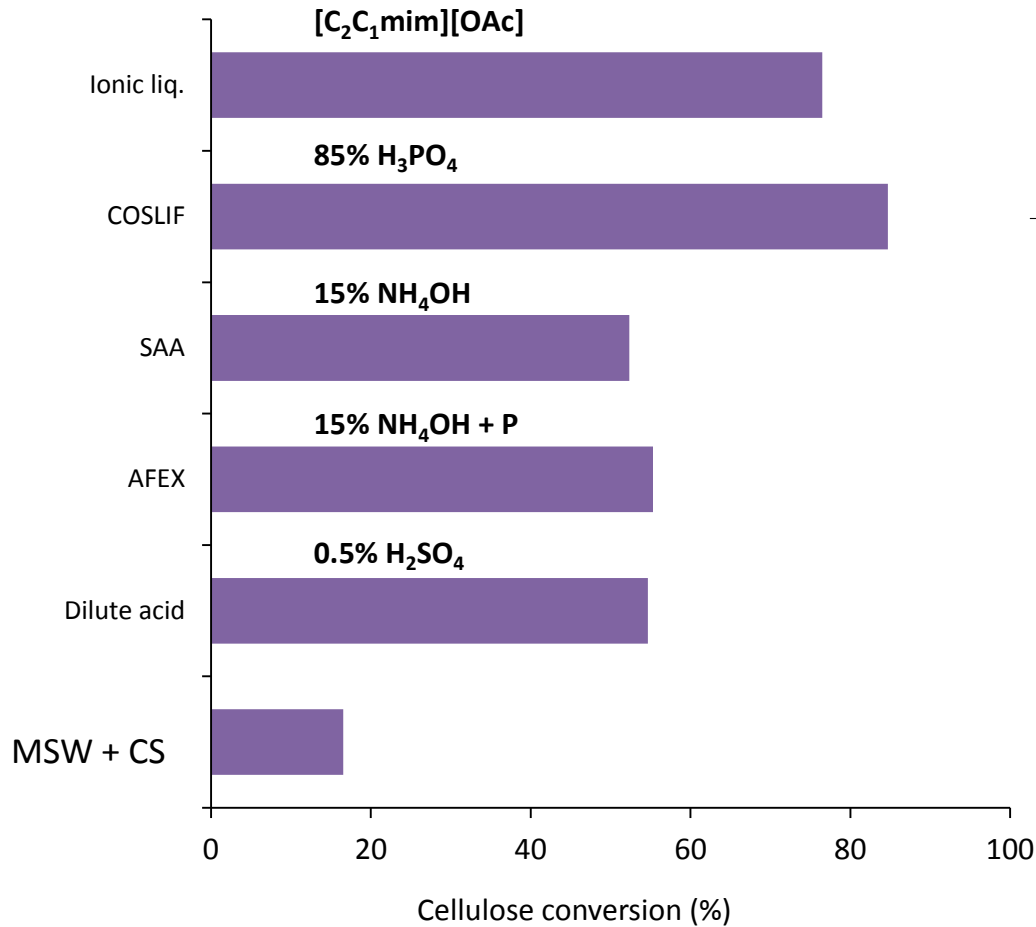
IOGEN®  
CORPORATION

DU PONT

DANISCO.

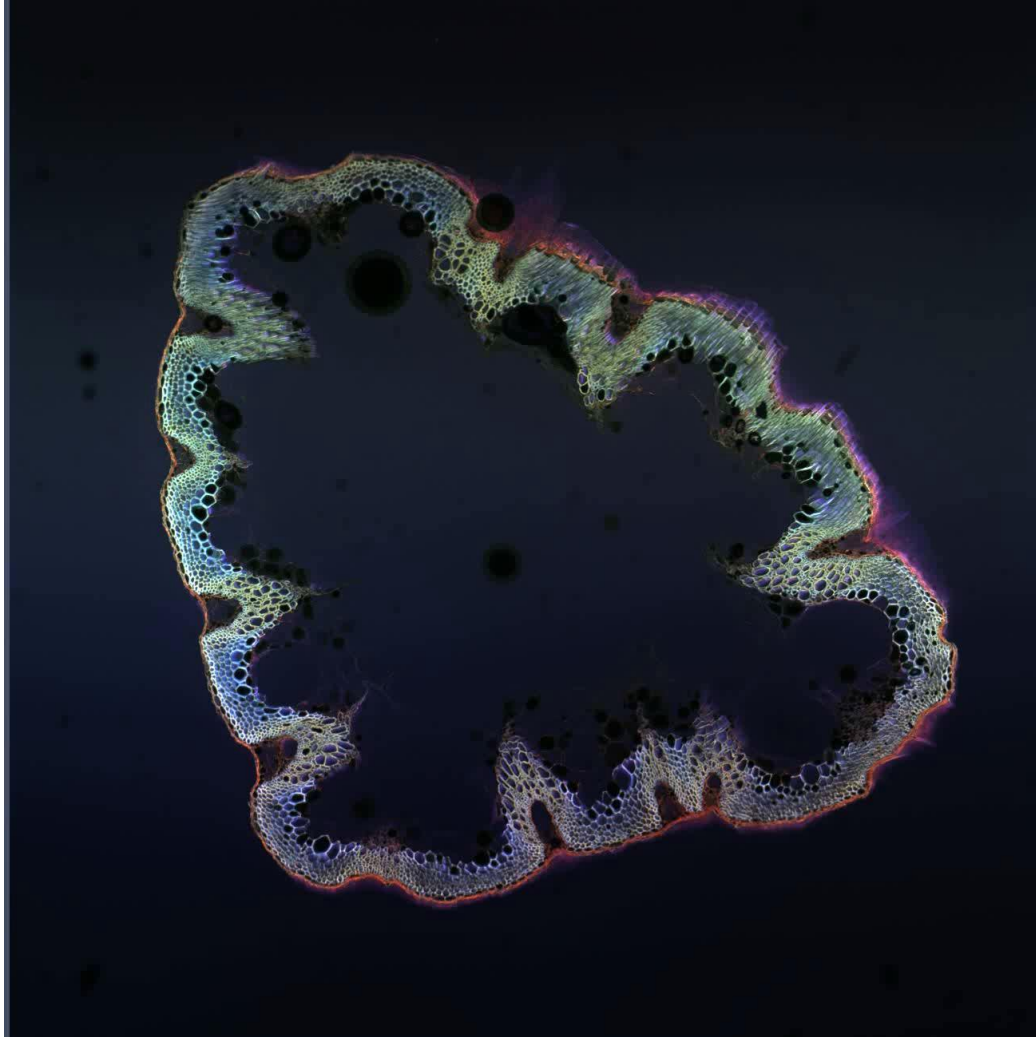
OF  
OPTAFUEL

# Biomass dissolution can enhance cellulose conversion



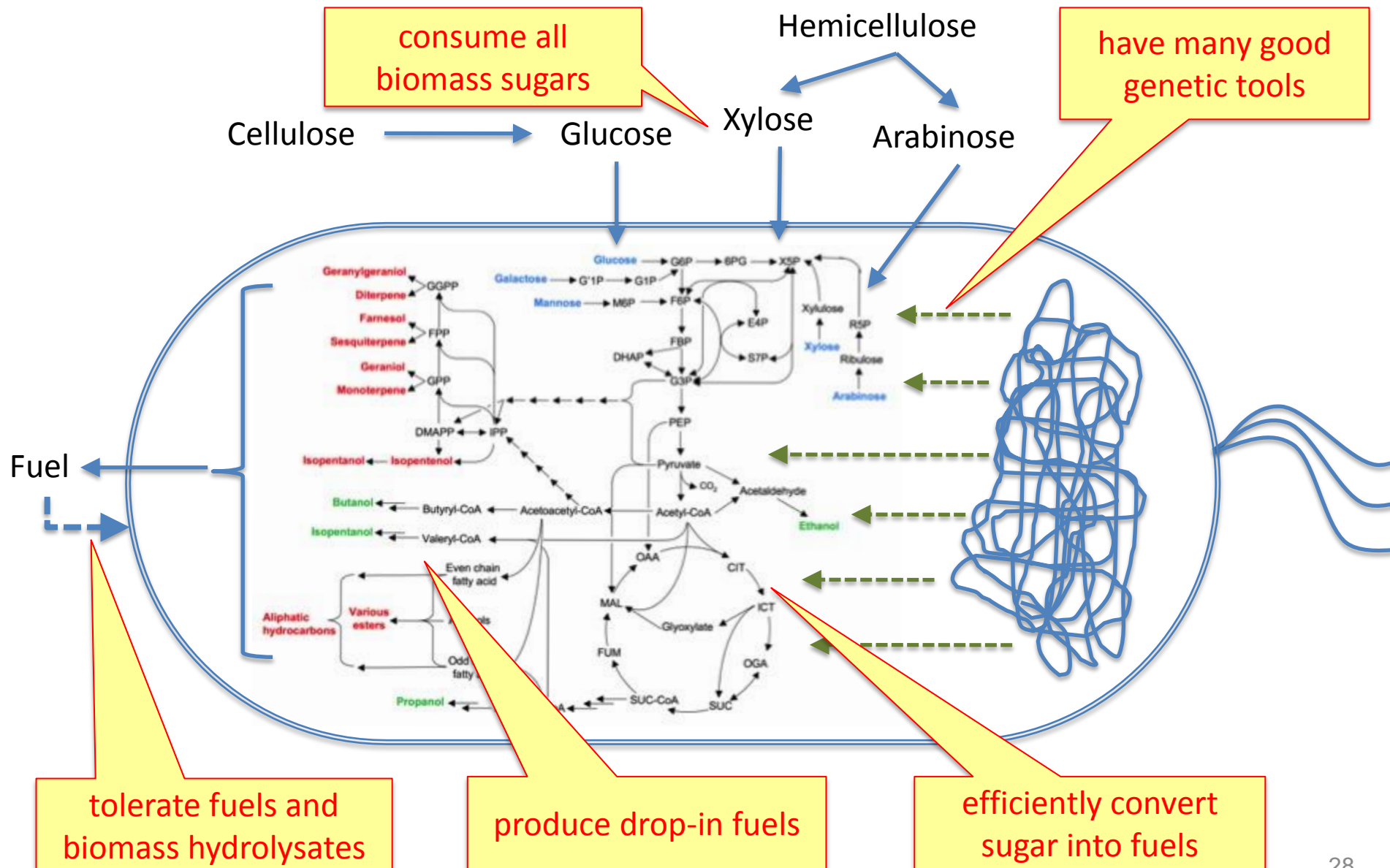
**Hydrolysis conditions:** Feed = 10% substrate, Cat. = 15 mg protein/g glucan,  $T = 50\text{ }^{\circ}\text{C}$ , pH 4.8, time = 24 h.

**Heterogeneity nature of paper makes it difficult to be dissolved and therefore hard to catalyze**



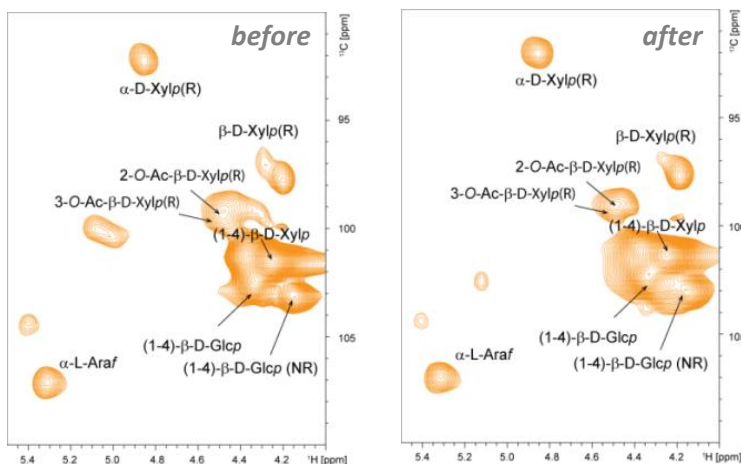
Switchgrass~200  $\mu\text{m}$

# The ideal biofuel-producing microorganism would.....

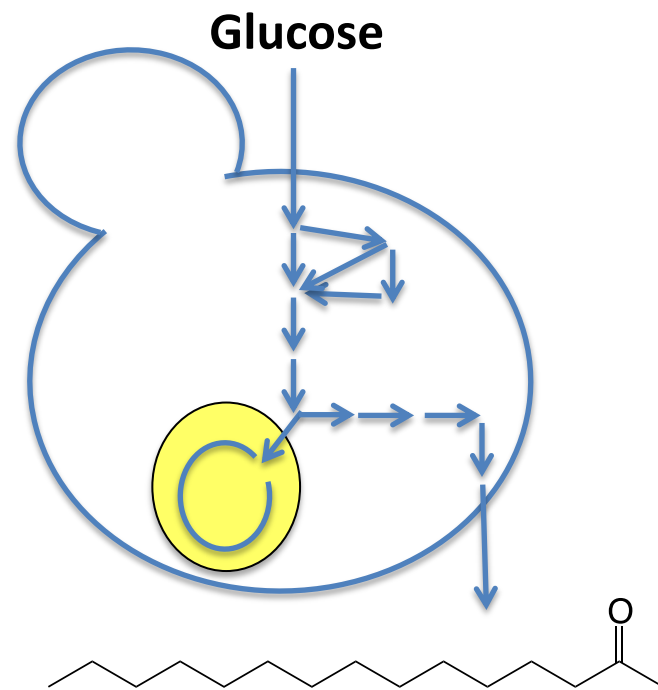
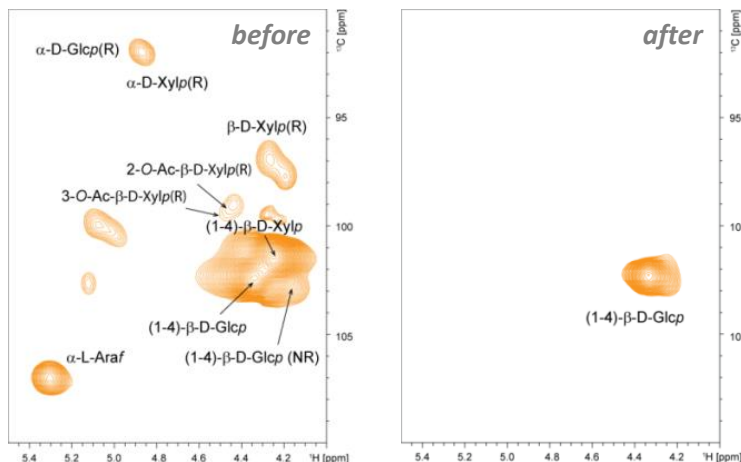


# HSQC can be applied in fermentation; it reveals how efficient substrate-microbe interaction is

## Untreated switchgrass



## Ionic liquid



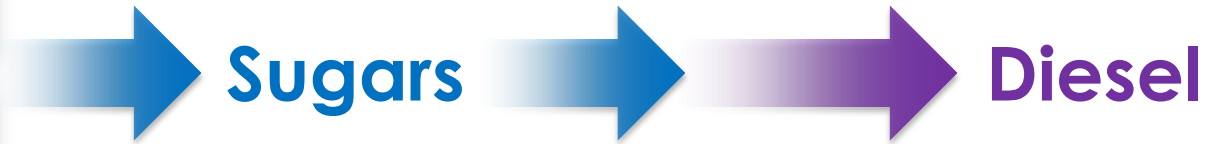
## Collaborators:

- Jana Muller (Calysta Energy)
- Harry Beller (Physical BioSciences)
- Jay Keasling (UC Berkeley)

# Summary



**Plant-based  
waste**



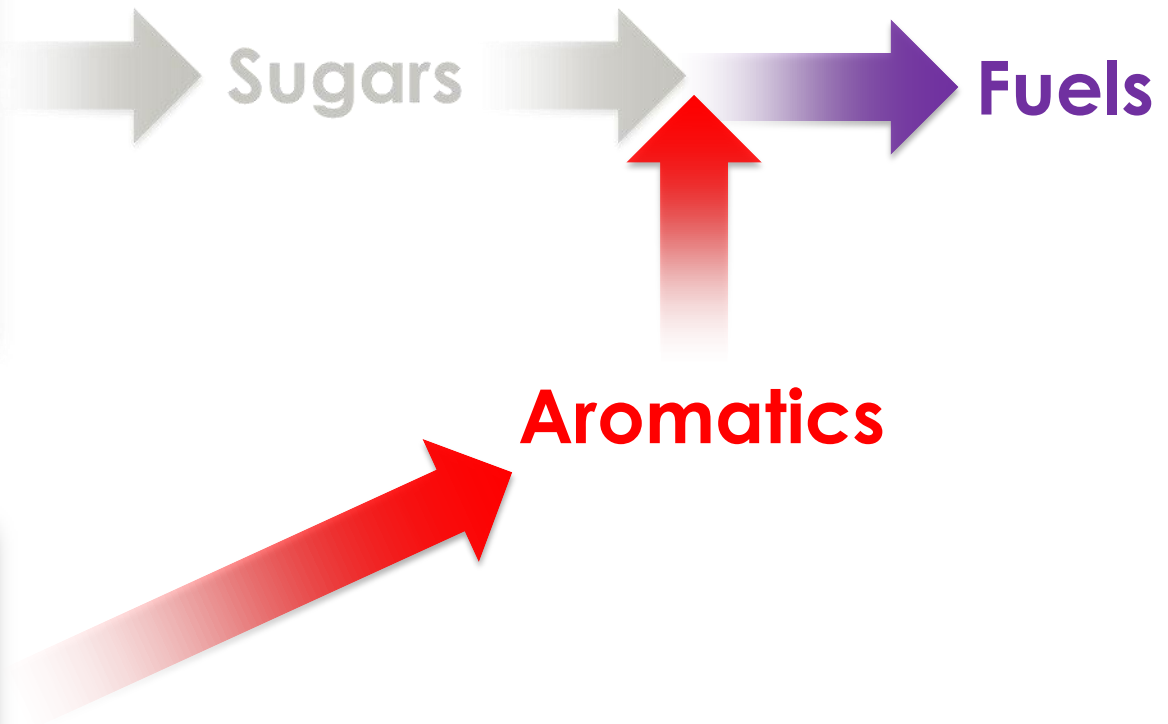
# Outline



Plant-based  
waste

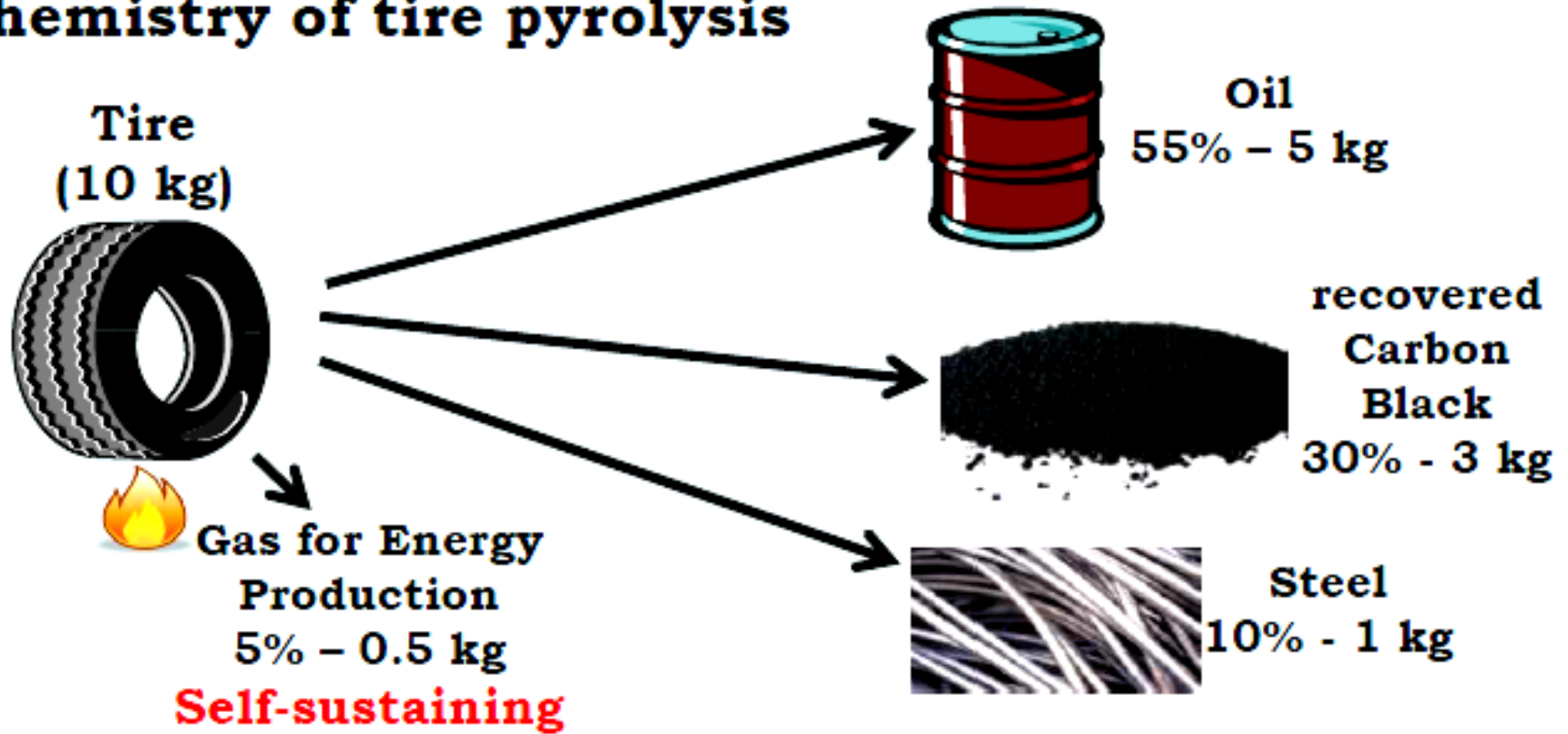


Tire waste

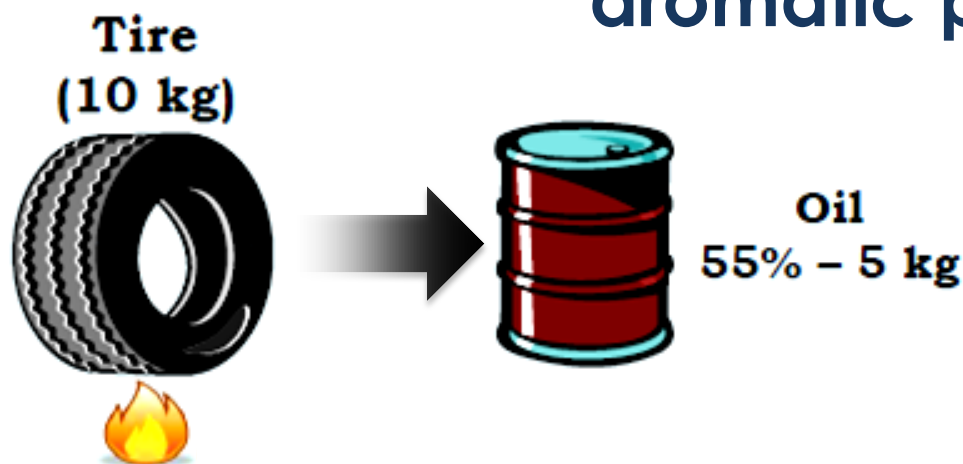


# Tires are currently under-utilized

## Chemistry of tire pyrolysis

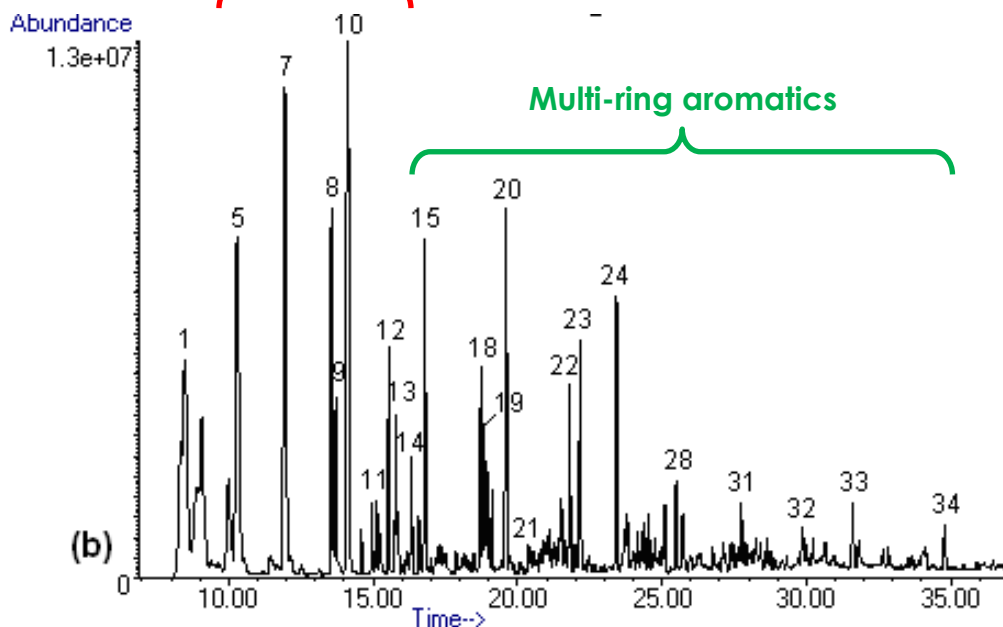


# Pyrolysis of waste tires yields a large amount of aromatic products



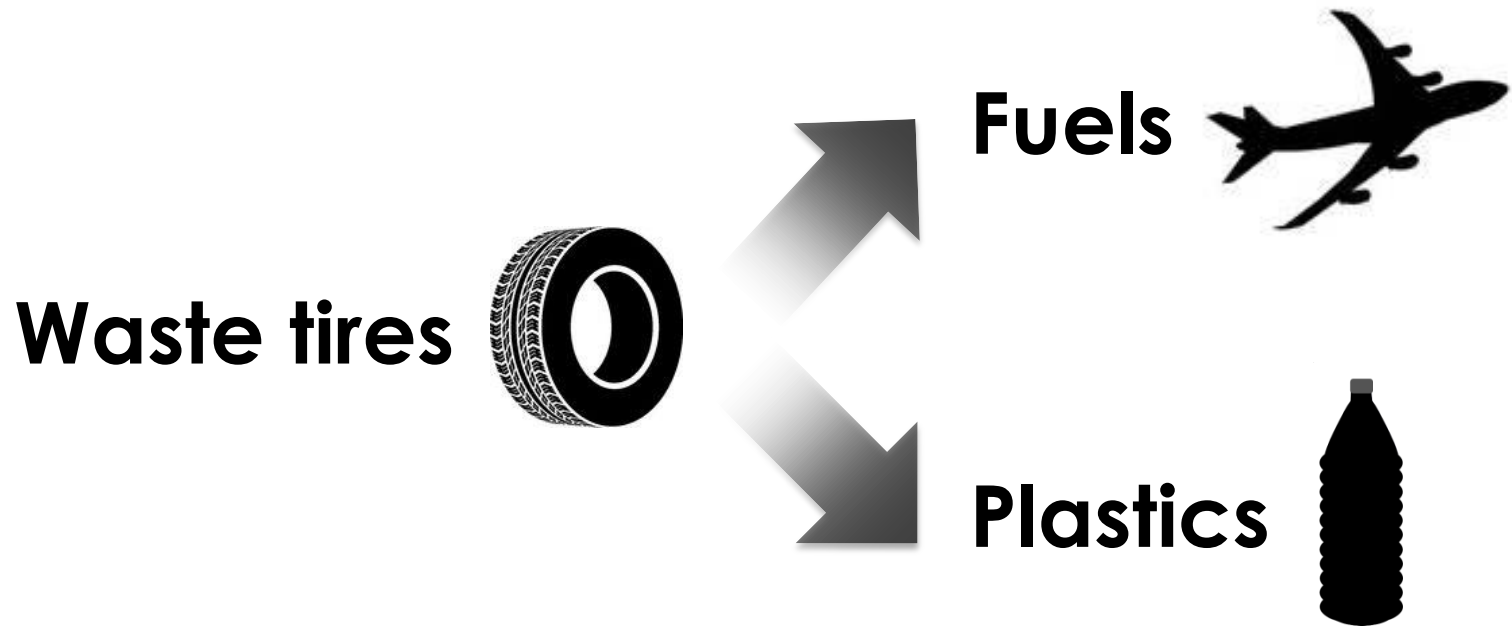
One-ring aromatics

Multi-ring aromatics

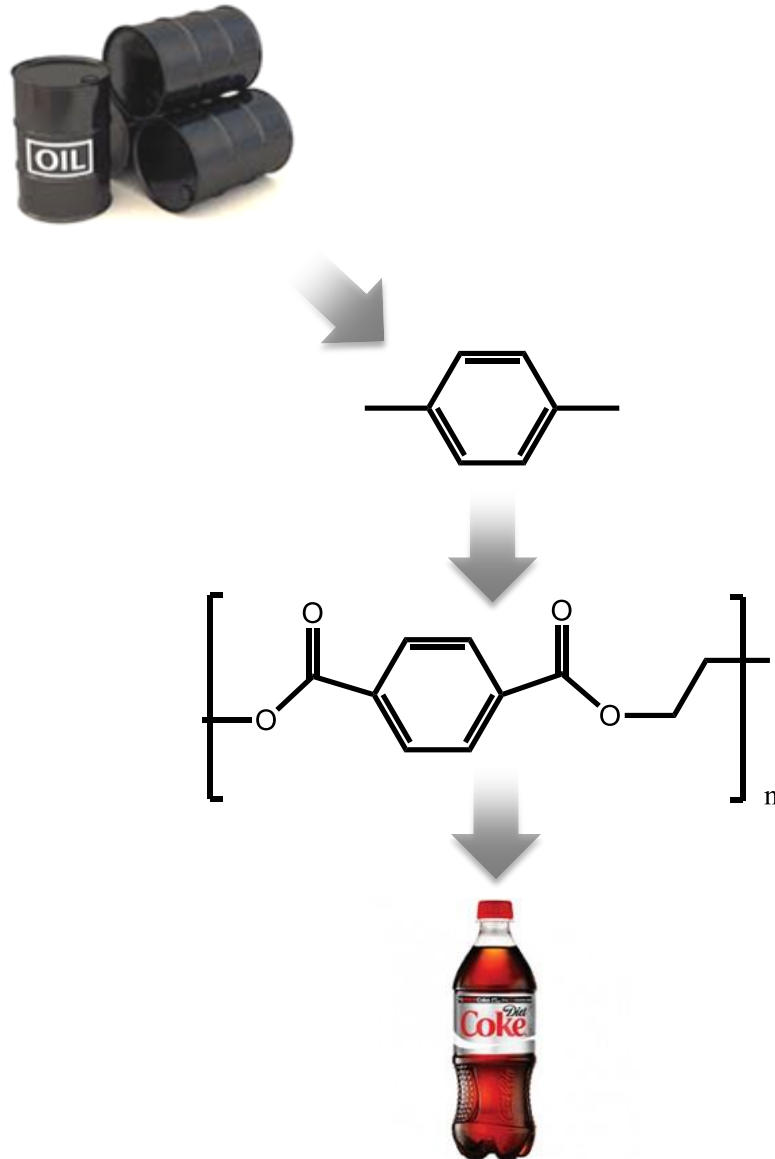


Peak	Retention time (RT) [min]	Pyrolysis products of the valve and the car tire rubbers at 700 °C
1	8.20	2-Butene
2	8.55	2-Methyl-1,3-butadiene
3	9.34	3-Methyl-2-pentene (isoprene)
4	9.75	5-Methyl-1,3-cyclopentadiene
5	10.08	Benzene
6	11.28	1-Methyl-1,4-cyclohexadiene
7	11.84	Toluene
8	13.51	Ethylbenzene
9	13.69	<i>p</i> -Xylene
10	14.08	Styrene
11	15.19	<i>m</i> -Ethyltoluene
12	15.52	<i>o</i> -Methylstyrene
13	15.81	1,2,4-Trimethylbenzene (pseudocumene)
14	16.28	1,2,3-Trimethylbenzene (hemimellitene)
15	16.78	Indene
16	17.43	<i>o</i> -Isopropenyltoluene
17	18.02	1,2,4,5-Tetramethylbenzene (durene)
18	18.75	3-Methylindene
19	18.86	2-Methylindene
20	19.58	Naphthalene
21	20.37	Benzothiazole
22	21.83	2-Methylnaphthalene
23	22.17	1-Methylnaphthalene
24	23.43	Biphenyl
25	24.06	Dimethylnaphthalene isomer
26	24.32	Dimethylnaphthalene isomer
27	24.43	Dimethylnaphthalene isomer
28	25.48	3-Methyl-1,1'-biphenyl
29	25.50	2,6-Bis-(1,1-dimethylethyl)-4-methylphenol (BHT)
30	26.52	1,6,7-Trimethylnaphthalene
31	27.75	Fluorene
32	29.88	1,2-Diphenylethylene (stilbene)
33	31.61	Anthracene
34	34.79	2-Phenylnaphthalene

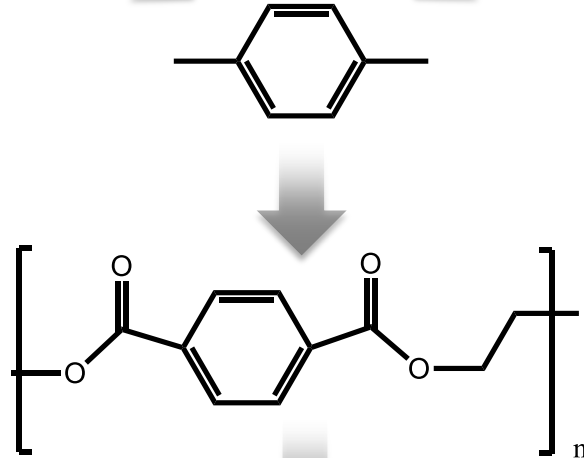
# Current efforts in the conversion of waste tires



# Currently *p*-xylene is produced from crude oil

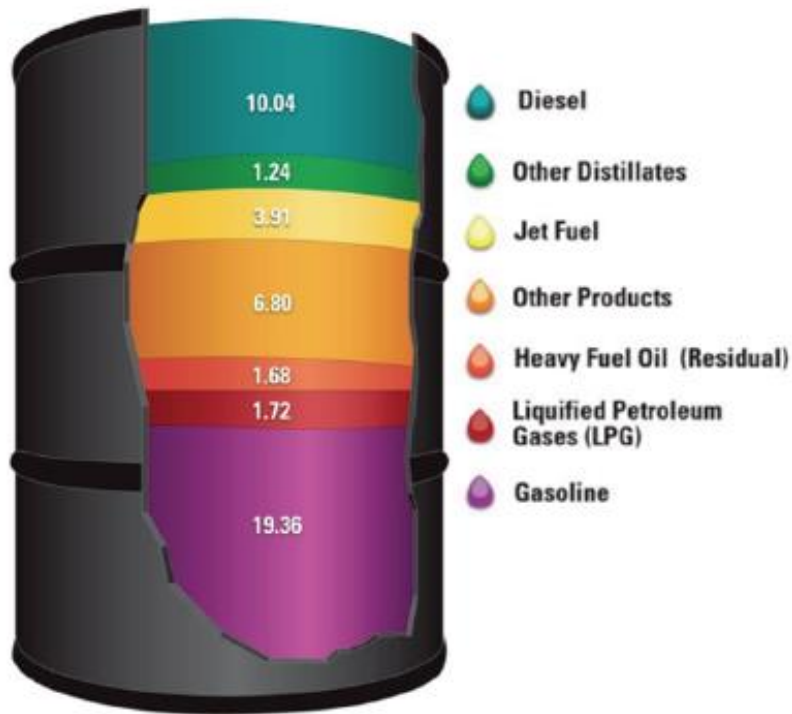


# Tires could potentially be a new *p*-xylene source

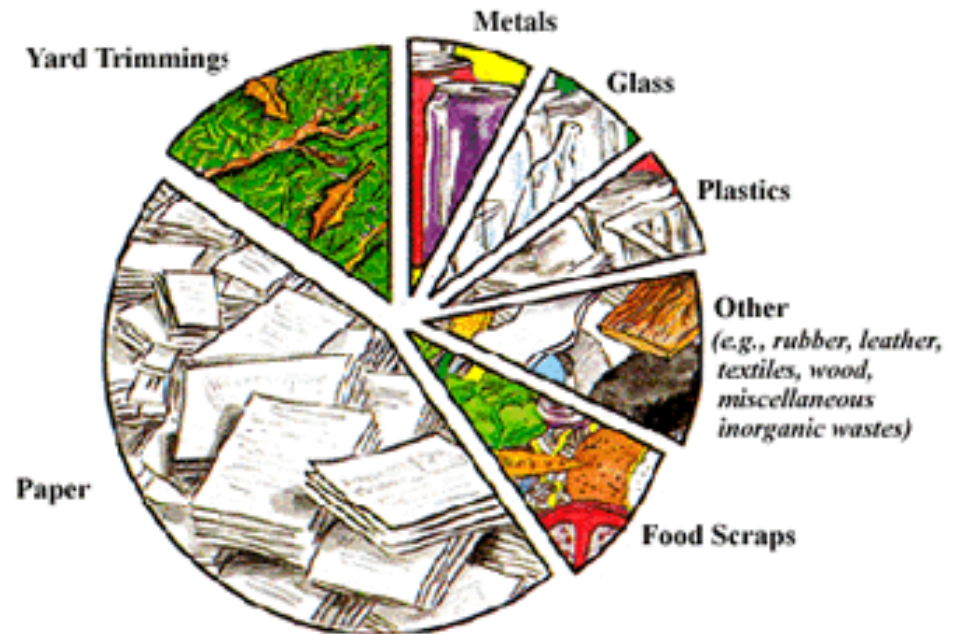


# MSW will become a new crude oil

## Petroleum



## Municipal solid waste



[Tikgroup.org](http://Tikgroup.org)

*'The Stone Age did not end because we ran out of stones; we transitioned to better solutions. The same opportunity lies before us with energy efficiency and clean energy'*

*-Steven Chu*